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RESEARCH NOTE

Photocatalytic Activity of TiO_2 Films Preserved under Different Conditions: The Gas-Phase Photocatalytic Degradation Reaction of Trichloroethylene

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The photocatalytic activity of TiO_2 films preserved under different conditions was investigated in the gas-phase photocatalytic degradation of trichloroethylene (TCE). The photocatalytic activity of the TiO_2 films was found to depend greatly on the preservation temperature and time. The TiO_2 films washed with water and then preserved at room temperature exhibited low photocatalytic activity compared with those that were unwashed. When the preservation time of the TiO_2 films was long, their photocatalytic activity decreased, irrespective of the preservation conditions. The catalyst that is deactivated due to the long preservation time can be regenerated by UV preillumination. © 2000 Academic Press

Key Words: **preservation; photocatalytic activity; TiO_2 films; trichloroethylene; UV preillumination.**

INTRODUCTION

Volatile organic compounds (VOCs) such as trichloroethylene (TCE) have been used in a wide range of industrial applications (1). Soil and groundwater have been polluted with these compounds discharged from improper industrial processes. Developments in the field of photocatalysis with a TiO_2 photocatalyst have led to the remarkable elimination of organic compounds, involving VOCs dissolved in water (2–5). On the other hand, the photocatalysis of TCE in the gas phase (6–10) showed high degradation rates compared with that in water (2, 11). Nimlos *et al.* (8) reported a specific chain reaction of the Cl radical in the TCE photocatalytic reaction in the gas phase, while its reaction in the aqueous phase was reported (11) to proceed via an OH radical.

In heterogeneous photocatalysis, photoinduced molecular transformation and reaction take place on the surface of the photocatalyst when the reactant is adsorbed under UV illumination (12). Therefore, the activity of the photocatalyst might be dependent on the surface conditions; the adsorbed species, other than reactant on the surface, may affect the reaction because they can hinder the adsorption of reactant. In particular, when the TiO_2 films coated on the substrate are repeatedly used in gas-phase photocatalysis, the pretreatment and preservation methods might significantly affect the photocatalytic activity. Sauer and Ollis mentioned the importance of catalyst deactivation (and regeneration) studies to clearly establish the process economics of photocatalyst technology (13). For these reasons, we reported the relation between the photocatalytic activities of the pretreated and untreated TiO_2 photocatalyst in the gas-phase photocatalysis of TCE (14). It has been found that UV preillumination of the TiO_2 surface before reaction was the most effective method to increase the photocatalytic activity among the tested pretreatments. This result showed that adsorbed species, such as water molecules, retard the reaction. However, the relation between the photocatalytic activity and preservation conditions of the photocatalyst has been studied little in the previous literature on gas-phase TCE photocatalysis.

In this paper, we report the effect of the preservation conditions of the photocatalyst on the gas-phase photocatalytic degradation of TCE using TiO_2 sol–gel films coated on glass plates (TiO_2-GP) as a photocatalyst.

METHODS

Photoreactor and experimental procedures. A batch reactor (125 ml) was used for the experiment (14, 15). It was designed for *in situ* measurement of the degradation reaction of TCE using Fourier Transform Infrared (FTIR) spectroscopy. The experimental procedures were as follows. (1) The TiO_2 films, washed with distilled water or unwashed, were preserved at room temperature (25°C;

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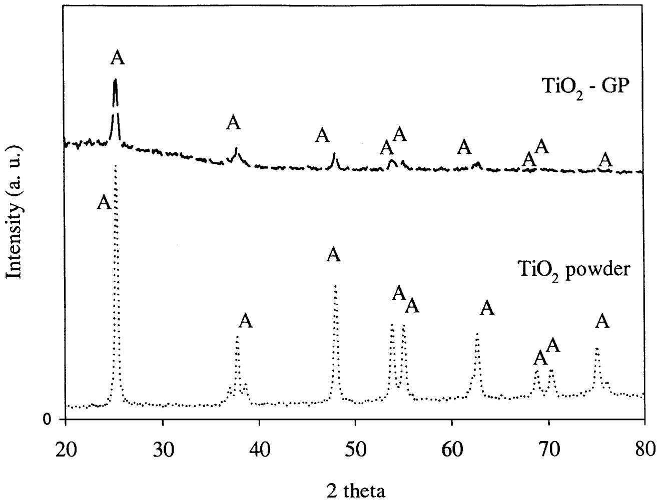

FIG. 1. XRD pattern of TiO_2 powder and TiO_2-GP (A: anatase phase).

relative humidity, 20–25%), or at 100°C for different periods of time; (2) the TiO_2 films were placed in the reaction chamber; (3) the atmosphere of the reaction chamber was substituted with dried air; (4) the concentration of TCE was adjusted to 4.6 mg liter^{-1}, and this concentration of TCE was used throughout the experiment. After the concentration of TCE had reached its equilibrium value, the degradation reaction of TCE was started. The temperature of the reaction chamber was kept at 25°C by air cooling. The photocatalyst was preserved at different conditions after the TCE was photocatalytically degraded to a level that was undetectable with an FTIR spectrometer.

Photocatalyst and light source. The TiO_2-GP (25×55 mm^2; BET surface area, <0.1 m^2 g^{-1}; thickness, 350 nm) was prepared by a sol–gel process. The sample was heated at 500°C for 3.5 h after being dipped 10 times. The prepared samples, TiO_2 powder and TiO_2-GP, were in the anatase phase (Fig. 1), and they were analyzed using an X-ray diffractometer (XRD: Rigaku D/Max-RC, 12 KW) with Cu $K\alpha$ radiation. A more detailed preparation method has been described in earlier reports (9, 16). Eight 20-W blacklight fluorescent lamps (Toshiba FL20S-BLB) were used as the light source, and their light intensity, measured with a light power meter (OPHIR-Laser Power Meter), was around 3.2 mW cm^{-2}.

Analysis. An FTIR spectrometer (Nicolet 800 FT-IR spectrometer) was used for the quantitative and qualitative determination of TCE and products (9). The peak height at 942 cm^{-1} for the C–Cl stretching vibration was used to determine the change in TCE concentration. A gas chromatograph (G-5000, HITACHI Co., Ltd.) equipped with an electron capture detector (GC-ECD) was also used to confirm the reaction products.

RESULTS AND DISCUSSION

To investigate the relation between the photocatalytic activity and preservation conditions of the TiO_2 films, the photocatalyst washed with water and the unwashed photocatalyst were preserved at room temperature or at 100°C in air. The degradation rate of TCE was very low at the initial stage of the reaction, and therefore the half-life of the reaction was calculated from the data concerning the variation of relative concentration of TCE as a function of illumination time. Figure 2 shows the half-life of the TCE degradation reaction as a function of preservation time at room temperature for the catalyst. The photocatalytic activity of the TiO_2 films washed with water was surprisingly low compared with the unwashed films. This result indicated that the photocatalytic activity might depend on the adsorbed species on the surface before the reaction. That is, when the TiO_2 films were washed with water, the surface might be covered with molecular water. However, when the unwashed TiO_2 films were used, the surface might be covered with nonvolatile reaction products. We have already reported that reaction products such as dichloroacetic acid ($CHCl_2COOH$, DCAA), which may be produced from dichloroacetyl chloride ($CHCl_2COCl$, DCAC), were detected on the TiO_2 surface after the TCE was destroyed (9), and molecular water adsorbed on the surface might retard the reaction (14, 16). Ollis *et al.* reported (17) that the rate of the gas-phase photocatalysis of TCE with Cl radicals was 10 to 100 times faster than that with OH radicals, and they proposed Cl radicals as the active species responsible for the rate enhancement.

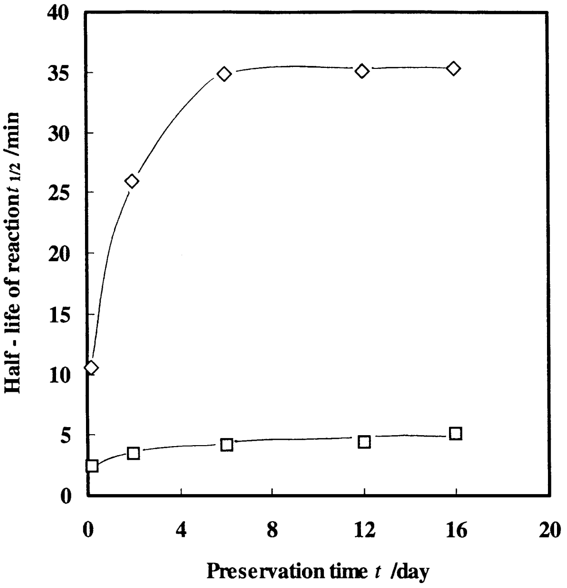

FIG. 2. Half-line of reaction as a function of preservation time of the catalyst. The TiO_2-GP was preserved at room temperature. (◇) TiO_2-GP washed with water; (□) unwashed TiO_2-GP.

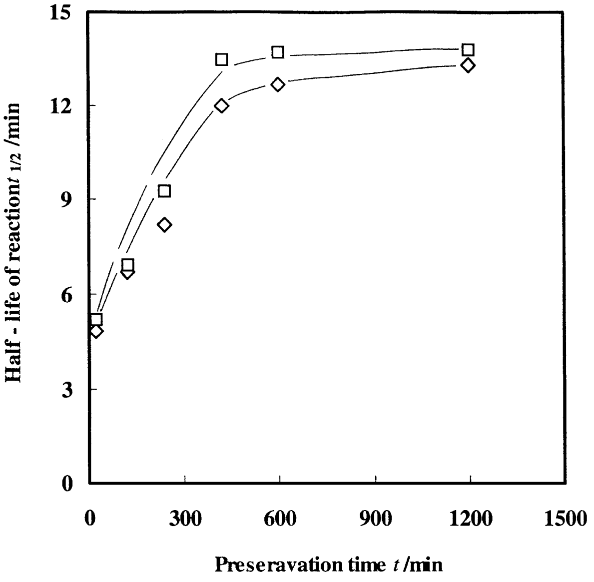

FIG. 3. Half-life of reaction as a function of preservation time of the catalyst. The TiO_2-GP was preserved at 100°C. (◊) TiO_2-GP washed with water; (□) unwashed TiO_2-GP.

On the other hand, the photocatalytic activity of the TiO_2 films, both washed and unwashed, decreased with an increase in their preservation time. The reason for this is now under consideration, but one possible explanation may be the adsorption of atmospheric contaminants on the surface during the long preservation time of the catalyst. This may result in a decrease of the active site and/or the prevention of the TCE adsorbing on the surface during the reaction.

Figure 3 shows the half-life of the reaction as a function of preservation time at 100°C for the catalyst. The change of half-life of the reaction when the catalyst washed with water was used agreed well with that for the unwashed catalyst. When this result was compared with that in Fig. 2, the degradation rates of TCE increased in the case of using the TiO_2 films washed with water and decreased in the case of using unwashed films. This might mean that most of the physisorbed water and reaction products remaining on the surface at room temperature preservation of the catalyst were desorbed when it was preserved at 100°C. Therefore, removal of the adsorbed species from the catalyst surface makes the reaction mechanism almost the same. From the results in Figs. 2 and 3, we can see that the photocatalytic activities of the TiO_2 films decreased with an increase of preservation time, irrespective of the preservation conditions. We confirmed, however, that the catalyst that had deactivated with an increase of preservation time was again regenerated (half-life of reaction ca. 2.2 min) by UV preillumination before reaction. This might be the result of all of the adsorbed species being removed from the surface as the result of UV preillumination. As for UV preillumination, it is described in detail elsewhere (14). Throughout the experiment, there were no differences in the reaction products.

When the preservation conditions of the catalyst were controlled, the reproducibility of the reaction was considerably improved. In addition, the photocatalytic activity of the TiO_2 films was maintained for more than two years without any deactivation following the proper pretreatment.

CONCLUSIONS

TiO_2 films preserved under different conditions were deactivated on increasing the preservation time. In particular, the photocatalytic activity differed considerably, depending on the preservation temperature of the photocatalyst. The photocatalytic activity of the TiO_2 films preilluminated before reaction was regenerated again even though the films were preserved under different conditions for a long time. The reproducibility of the reaction was significantly improved when the preservation conditions of the catalyst were controlled.

REFERENCES

1. Kochany, J., and Bolton, J. R., *Environ. Sci. Technol.* **26**, 262 (1992).
2. Ollis, D. F., *Environ. Sci.Technol.* **19**, 480 (1985).
3. Al-Ekabi, H., and Serpone, N., *J. Phys. Chem.* **92**, 5726 (1988).
4. Kormann, C., Bahnemann, D. W., and Hoffmann, M. R., *Environ. Sci. Technol.* **25**, 495 (1991).
5. Murabayashi, M., Itoh, K., Kuroda, S., Huda, R., Masuda, R., Takahashi, W., and Kawashima, K., *Denki Kagaku* **60**, 741 (1992).
6. Dibble, L. A., and Raupp, G. B., *Catal. Lett.* **4**, 345 (1990).
7. Kutsuna, S., Ebihara, Y., Nakamura, K., and Ibusuki, T., *Atmospheric Environ.* **27**, 599 (1993).
8. Nimlos, M. R., Jacoby, W. A., Blake, D. M., and Milne, T. A., *Environ. Sci. Technol.* **27**, 732 (1993).
9. Kim, J. S., Itoh, K., and Murabayashi, M., *Chemosphere* **36**, 483 (1998).
10. Peral, J., and Ollis, D. F., *J. Catal.* **136**, 554 (1992).
11. Ollis, D. F., Hsiao, C. Y., Budiman, L., and Lee, C. L., *J. Catal.* **88**, 89 (1984).
12. Trillas, M., Peral, J., and Domenech, X., *Appl. Catal. B Environ.* **3**, 45 (1993).
13. Sauer, M. L., and Ollis, D. F., *J. Catal.* **163**, 215 (1996).
14. Kim, J. S., Itoh, K., Murabayashi, M., and Kim, B. A., *Chemosphere* **38**, 2969 (1999).
15. Kim, J. S., Itoh, K., and Murabayashi, M., *Denki Kagaku* **64**, 1200 (1996).
16. Kim, J. S., Itoh, K., and Murabayashi, M., *Denki Kagaku* **65**, 966 (1997).
17. D'Hennezel, O., and Ollis, D. F., *Stud. Surf. Sci. Catal.* **101**, 435 (1996).